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DIFFUSION COEFFICIENT MEASUREMENTS
FOR GAS MIXTURE OF ATOMIC
AND MOLECULAR HYDROGEN

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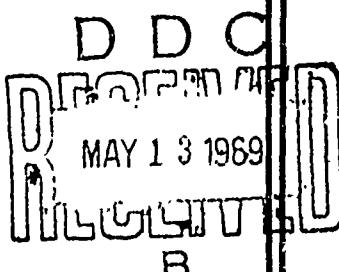
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TABLE OF CONTENTS

LIST OF TABLES

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OF ATOMIC AND MOLECULAR HYDROGEN*

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ABSTRACT

The multicomponent diffusion coefficient D_{H,H_2} has been evaluated from measurements of the relative atom density in a semi-infinite catalytic cylinder as a function of (a) distance from the atom source under steady-state conditions, and (b) time during the transient condition associated with removal of the atom source after attainment of steady state. An electron spin resonance spectrometer was employed for atom-density measurements and a radio-frequency discharge for atom production in the total gas-pressure range from 0.85 to 2.6 torr. The value for the diffusion coefficient was found to be $D_{H,H_2} = 1.8 \pm 0.13 \text{ cm}^2 \cdot \text{sec}^{-1}$ at 1 atmosphere and $293 \pm 3\,^{\circ}K$. Experimental data for the variation of D_{H,H_2} as a function of temperature (293 to $719\,^{\circ}K$) are analyzed in terms of different interaction potentials for the atom-molecule collision.

INTRODUCTION

A number of publications[1,2,3] have dealt with the theoretical calculation of the binary diffusion coefficient of atomic hydrogen in molecular hydrogen (D_{H,H_2}). Also an estimate of this parameter has been made from viscosity measurements[4,5] on the basis of theoretical interaction potentials. However no direct determination of the binary diffusion coefficient has been reported to ascertain the degree of validity of the theoretical analyses, which involve calculations based on multiple interaction potentials for species with unfilled electronic shells.[6]

In a preceding publication we demonstrated the feasibility of measuring diffusive transport coefficients by a combination of steady-state and transient experiments.[7] We have applied the principle of this method to the study of D_{H,H_2}.

APPARATUS

The diffusion coefficient of hydrogen atoms in hydrogen was measured by means of the apparatus shown schematically in Fig. 1. The central part of the vacuum apparatus is a quartz diffusion tube 9.4 mm i.d. which includes a constriction 2 mm i.d. and 3 mm long. On one side of the constriction the tube (45 cm in length) passes through the ESR cavity. The quartz section is attached by means of an "O" ring gland to a pyrex tube (10 mm i.d. and 50 cm in length) on the end of which is a pressure gauge (Autovac pirani tube). On the other side of the constriction the quartz tube passes through an rf discharge coil and a liquid nitrogen trap (6 mm i.d., 50 cm from the constriction). This end of the apparatus communicates with the rest of the vacuum system comprising metal valves, a McLeod gauge for pressure calibration, and the supply of hydrogen.

The hydrogen (Matheson & Company, prepurified grade, purity >99.95%) was passed through a de-oxo purifier and two traps cooled by liquid nitrogen before entering the apparatus. For cleaning, the glass tubing was exposed successively to concentrated nitric acid, concentrated hydrochloric acid, 10% hydrofluoric acid, and chromic acid-sulfuric acid

cleaning solution. Finally the tube was rinsed with large quantities of distilled water. The last solution was tried in an attempt to change the activity of the quartz walls for hydrogen atom recombination. The treatment resulted in a decrease of catalytic activity by a factor of about two.

The rf discharge was excited by inductive coupling to an 18 mc/sec transmitter, and the region of the rf coil was cooled by a fan. The center of the rf coil, around the quartz tube, was located about 7 cm from the constriction and about 25 cm from the center of the magnet. This configuration provided satisfactory atom densities in the diffusion tube. Also it prevented the plasma from extending beyond the constriction. At low pressure and low rf power, a Tesla coil was required to initiate the discharge for the transient experiments.

For the transient measurements the pulsing of the discharge, the initiation of the Tesla coil, and the triggering of the time-averaging computer (Varian C1024) were synchronized. The time basis for these measurements was obtained from an electromechanical timer (Flexopulse, Eagle Signal Corp.), with which ON- and OFF-time of the discharge could be adjusted independently. This timer operated a mercury relay, one pole of which keyed the transmitter. Another pole of the mercury relay operated an auxiliary circuit that turned the Tesla coil ON for 0.1 sec at the time the transmitter was turned ON. Operation of the Tesla coil was limited to as short a period as possible in order to avoid electrical interference with the sensitive electronic measurement devices. Since the surface-catalyzed recombination of atomic hydrogen is a reaction of first-order in gas atom density, measurements of relative atom densities are adequate for the evaluation of the surface activity and the diffusion coefficient.

For determination of relative hydrogen atom density and its rate of decay in the transient experiments, we employed an electron spin resonance (ESR) spectrometer (Varian V-4502, X-band) equipped with a 12-in. magnet and a time-averaging computer. The magnetic field was controlled by a Fieldial (Varian Mark I) for the steady-state measurements. Since the Hall effect sensor of the Fieldial was sensitive to the rf field of the

3

discharge, current-regulation of the magnetic field was needed during transient measurements. A rectangular cavity (TE_{102}) was attached to the low power connection of the microwave bridge. The microwave power was adjusted for maximum signal intensity. A modulation frequency of 100 kc/sec was employed, and the modulation amplitude was adjusted for maximum signal intensity which also provided substantial line broadening (8 Oe) so that during the transient measurement any fluctuations in the magnetic field were not significant.

A chip of ruby was affixed to one inside wall of the cavity to provide a monitor for its sensitivity as it was moved along the quartz tube. Movement of the cavity was achieved by simply sliding the microwave bridge, with its attached waveguide leading to the cavity, on the horizontal table mounted above the magnet. This procedure permitted a horizontal cavity movement of 7 cm with a variation of reference signal intensity of less than 1.5%; greater movement resulted in line distortion due to inhomogeneous magnetic fields.

EXPERIMENTAL DETAILS AND RESULTS

A. Transient Measurement

The transient experiments involved study of the rate of atom density decay from the steady-state value at a given point in the cylindrical reactor after rapid extinction of the atom source. For the determination of the atom density, the magnetic field was adjusted for a peak of the ESR derivative signal and the transient decay was time-averaged by cycling the discharge with an ON-time of 2 sec and an OFF-time of 1 sec. Collection of the experimental data was begun after exposure of the apparatus to the discharge cycling for a period of 15 min. At a given pressure the power input into the rf discharge was adjusted to a level adequate for atom detection, yet low enough to make the atomic species the minor component of the gas mixture. The cavity was situated as close to the constriction as possible in order to obtain the highest atom density. However, the distance between the cavity center and the constriction could not be less than 15 cm, a distance dictated by a compromise.

4

between the interaction of the magnet with the plasma and the limitations of magnetic field homogeneity. In order to obtain an adequate signal-to-noise ratio for the transient measurement of hydrogen atom decay, the results of about 100 experiments were averaged on the computer. The electrical time constant associated with the ESR signal to the computer was adjusted to 1 msec, which is less than 5% of the time for $1/e$ decay of the signal; the decay rate was unaffected by shorter electrical time constants.

Typical transient decays of logarithm of the relative atom density versus time are shown in Fig. 2 for several pressures. For convenience the atom densities in the figure have been normalized at time zero because the relative atom densities depended not only on the pressure but also on the rf power, which was adjusted to a convenient value.

B. Steady-State Measurement

For the determination of the atom density gradient along the length of the quartz diffusion tube, the rf discharge was operated continuously and the atom density was recorded for various positions of the cavity along the tube. At a given pressure, measurements were made after the atom density at some position, x, was constant. Usually a steady-state condition occurred after about 10 mins.

The steady-state data obtained at the pressures corresponding to the transient measurements of Fig. 2 are plotted in Fig. 3. The linear relationships between logarithm of atom density and distance x at given pressures satisfy the requirements of the theory for an infinite tube with catalytic walls for which the heterogeneous atom recombination is first order in atom density. The linearity of the curves further establishes uniformity of the wall activity along the tube. The magnitude of the slopes are labeled on each curve (Fig. 3). They are found to be proportional to the square root of the total pressure in accordance with theory.[8]

5

THEORETICAL ANALYSIS

The mathematical analysis requires the steady-state and transient solutions for a reacting system involving a cylinder of infinite length and diffusion of a reactant (present at low concentrations) as a result of a catalytic reaction by first-order heterogeneous kinetics. The transport equation in cylindrical coordinates applicable to this problem reads[9]:

$$D(n_{xx} + \frac{2}{r} n_r + n_{xx}) = n_t \quad , \tag{1}$$

where D is the diffusion coefficient, n the atom density (in the gas phase), and r the radical coordinate in the cylindrical reactor of radius R.

The boundary conditions are:

$$n(r,o,t) = o \quad \text{for } t > o \text{ at } x = o \tag{2}$$

$$n \rightarrow o \quad \quad \text{as } x \rightarrow \infty \tag{3}$$

$$n_r(o,x,t) = o \quad \quad \text{at } r = o \tag{4}$$

$$n_r(R,x,t) + \frac{1}{\delta R} n(R,x,t) = o \quad \quad \text{at } r = R, \tag{5}$$

where δ represents a dimensionless parameter involving the catalytic efficiency γ of the cylinder walls

$$\delta = [4D/(\gamma CR)][(2-\gamma)/2] \quad , \tag{6}$$

with $0 \leqslant \gamma \leqslant 1$, and C, the mean atomic velocity of the reactant.

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[9]The subscripts denote derivative with respect to the axial direction (x), the radial (transverse) direction (r), and time (t).

The boundary condition given by Eq. (2) specifies the existence of a strong "sink" in the region of the atom source at $t > o$, a condition prevailing during our experimental measurements. The quartz walls warmed by exposure to the rf discharge and the liquid nitrogen trap in close proximity to the discharge act as efficient atom sinks[10] and cause rapid decay in atom density as soon as the discharge is turned off.

The initial condition for the time-dependent solution is given by the steady-state atom distribution in the cylinder[8]

$$n^*(r,x) = \sum_{i=1}^{\infty} A_i \, J_0(\xi_i r) \, \exp(-\xi_i x) \quad , \tag{7}$$

where

$$A_i = 2 \, n_0 / \left\{ R \, \xi_i^2 (1 + \delta^2 R^2 \xi_i^2) \, J_1(\xi_i R) \right\} \quad , \tag{8}$$

with n_0 the atom density at $x = o$, and ξ_i ($i = 1,2,3. \quad .$), the positive roots of the Bessel-function equation

$$J_0(\xi R) = \delta \, R \, \xi \, J_1(\xi R) \quad . \tag{9}$$

By mathematical methods similar to those described in reference 7 one finds the transient solution

$$n(r,x,t) = \frac{1}{2} \sum_{i=1}^{\infty} A_i F_i(x,t) \, J_0(\xi_i r) \quad , \tag{10}$$

with A_i defined by Eq. (8) and

$$F_i(x,t) = -\exp(\xi_i x) \, \mathrm{erfc} \left[\xi_i \sqrt{Dt} + \frac{x}{2 \sqrt{Dt}} \right]$$

$$+ \exp(-\xi_i x) \, \mathrm{erfc} \left[\xi_i \sqrt{Dt} - \frac{x}{2 \sqrt{Dt}} \right] \quad . \tag{11}$$

The value of n averaged over the cross section of the tube is found to be:

$$\bar{n}(x,t)/n_0 = 2 \sum_{i=1}^{\infty} F_i(x,t) / [R^2 \xi_i^2 (1 + \delta^2 R^2 \xi_i^2)] \quad . \tag{12}$$

7

For conditions where the one-term approximation of Eq. (12) is applicable and the value of δ is large (low catalytic activity and/or high diffusion coefficient) Eq. (12) reduces to

$$\bar{n}(x,t)/n_0 = \tfrac{1}{2}\left\{-\exp(\tfrac{K}{D})^{\frac{1}{2}} \ \text{erfc}\ (\sqrt{Kt} + \frac{x}{2\sqrt{Dt}})\right.$$

$$\left. + \exp[-(\tfrac{K}{D})^{\frac{1}{2}}]\ \text{erfc}\ (\sqrt{Kt} - \frac{x}{2\sqrt{Dt}})\right\}\ , \qquad (13)$$

where the quantity $\zeta_1 = (2/\delta R^2)^{\frac{1}{2}} = K/D$, with K representing the rate constant for the first-order surface reaction ($K = 2D/\delta R^2 = \gamma c/2R$). Also it is found that at long times, $t \gg 1/K$, and large values of the arguments in the complementary error function, the relative reactant decay becomes an exponential function of time

$$\bar{n}(x,t)/n_0 \simeq [x/(Kt\sqrt{\pi Dt})\ \exp\ (-Kt)\ . \qquad (14)$$

Similarly for moderately active cylinder walls the steady-state solution yields

$$\bar{n}^*(x)/n_0 \simeq \exp\ [-(K/D)^{\frac{1}{2}}]\ x\ . \qquad (15)$$

DISCUSSION

The preceding theoretical analysis shows that the combination of transient and steady-state measurements yields the parameter D_{ij}. In the system under examination, the experimental results for the variation of atom density with time (after termination of reactant input into the system) and with distance (from the source) were analyzed by means of Eqs. (13) and (15). The condition $t \gg 1/K$, which applies to the approximate solution expressed in Eq. (14), would have required atom-density measurements at $t \gg 1$ sec with atom densities so small as to make the detector output from the ESR signal too low relative to the noise level of the apparatus.

In the calculation of the binary diffusion coefficient we use the value of K/D obtained from the steady-state measurements and compute the atom density for each of a number of values of Dt, i.e., n as a function of

Dt, by means of Eq. (13). The transient experiment yields the time of occurrence of each of these atom densities $n(t)$, which by substitution into the $n(Dt)$ values provide the parameter D. The values of D so obtained for a series of points on the experimental $n(t)$ curve exhibit a deviation of less than 10% from the average value. A typical example of the calculated transient atom density employing an average value of D is shown in Fig. 4. The diffusion coefficients derived from the measurements at the various total gas pressures are summarized in Table I. The average value of D_{H,H_2} at 293 $\pm$ 3°K and 1 atmosphere is found to be 1.80 ± 0.13 cm²·sec⁻¹.

The relative changes in D_{H,H_2} as a function of temperature reported in reference[11] may now be converted into absolute values based on results presented in this study. The data span a temperature range from 293°K to 719°K (Table II). They allow comparison with various theoretical analyses of the transport coefficients of the H,H_2 system. The data shown in Fig. 5 compare the experimental diffusion coefficients with recent semiempirical calculations by Weissman and Mason[3] on the basis of a modified Buckingham interaction potential (exp-6; $\epsilon/k = 16.7$°K; $r_m = 3.847$ Å; and $\alpha = 12.45$). The theoretical values of D_{H,H_2} fall on a curve (dashed line, Fig. 5) well above the experimental one at elevated temperatures. By adjusting the magnitude of the parameter r_m to a value of 3.90 Å in the (exp-6) potential function (solid line, Fig. 5), much closer agreement can be obtained. Also it should be noted that the measured value of D_{H,H_2} at 293°K is in satisfactory agreement with one derived from recent viscosity measurements[5] for the H,H_2 system and analyzed in terms of the same (exp-6) interaction-potential.

The experimental results obtained under steady-state conditions (Fig. 3) lend themselves to an evaluation of the catalytic surface activity of the quartz walls for hydrogen-atom recombination. The steady-state axial atom decay is an exponential function of the distance from the source (Eq. 15) and, on a semilogarithmic plot, the slope is proportional to $(K/D)^{\frac{1}{2}}$. An analysis of the data is summarized in Table III. The value of $\gamma = 1.8 \times 10^{-5}$ for quartz is considerably lower than that reported

9

for Pyrex,[10] but it is of the same magnitude as that for silica at room temperature.[12]

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Table I. Experimental values of binary diffusion coefficient in H, H_2 system at $293 \pm 3^\circ K$.

Total pressure torr	D_{H,H_2} cm$^2 \cdot$sec^{-1}	$D_{H,H_2} \cdot P$ atm$\cdot$cm$^2 \cdot$sec^{-1}
0.85	1540	1.73
1.43	795	1.50
2.10	698	1.92
2.15	590	1.67
2.56	530	1.81
		$\langle$ Av. = 1.80 $\pm$ 0.13 $\rangle$

Table II. Diffusion coefficients of the H,H_2 system at elevated temperatures.

Temp °K	$D_{H,H_2} \cdot P$ (atm·cm²·sec⁻¹)	
	relative[a]	absolute
293	1.00	1.80[b]
349	1.29	2.32
372	1.67	3.01
375	1.42	2.56
422	1.76	3.16
455	2.25	4.05
498	2.14	3.86
518	2.60	4.68
666	3.10	5.58
719	4.10	7.39

[a]H. Wise, J. Chem. Phys., 34, 2139 (1961).

[b]this paper.

Table III. Catalytic surface activity of quartz for hydrogen atoms
at $293^{\circ}K$.

| P (torr)	D ($cm^2 \cdot sec^{-1}$)	$(K/D)^{\frac{1}{2}}$ (cm)	K (sec^{-1})	$\gamma(\times 10^5)$
0.85	1540	0.060	5.5	2.0
1.43	795	0.076	4.6	1.8
2.10	698	0.086	5.0	1.9
2.15	590	0.085	4.3	1.6
2.56	530	0.092	4.1	1.6
				$\langle$ Av. = 1.8 $\rangle$

List of Figures

Figure 1   SCHEMATIC DIAGRAM OF APPARATUS
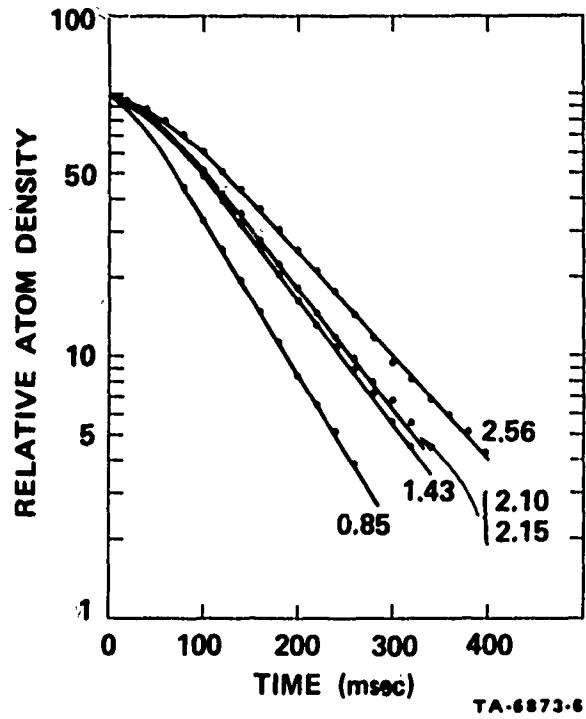
TA:6873-9

Figure 2   TRANSIENT DECAY OF HYDROGEN
            ATOMS AT VARIOUS TOTAL GAS
            PRESSURES (x = 15 cm)
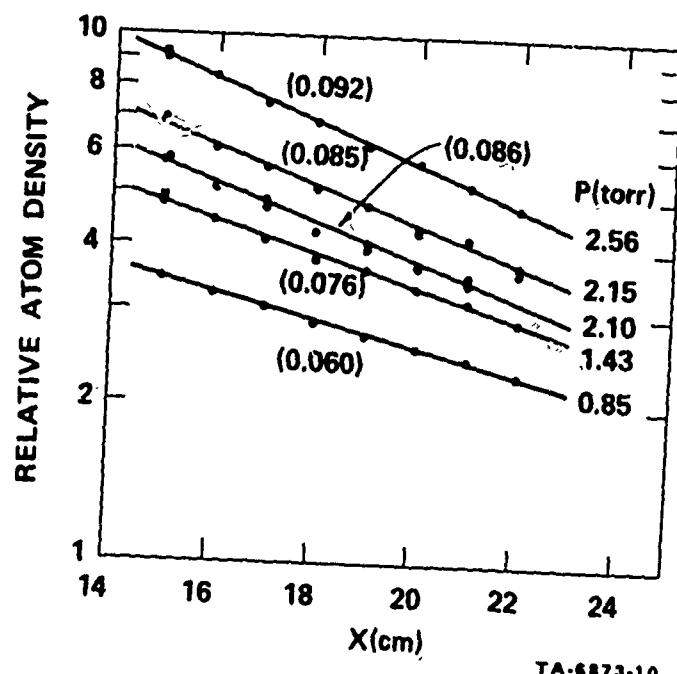
Figure 3   STEADY-STATE ATOM-DENSITY PROFILE
AS A FUNCTION OF DISTANCE FROM
THE ATOM SOURCE
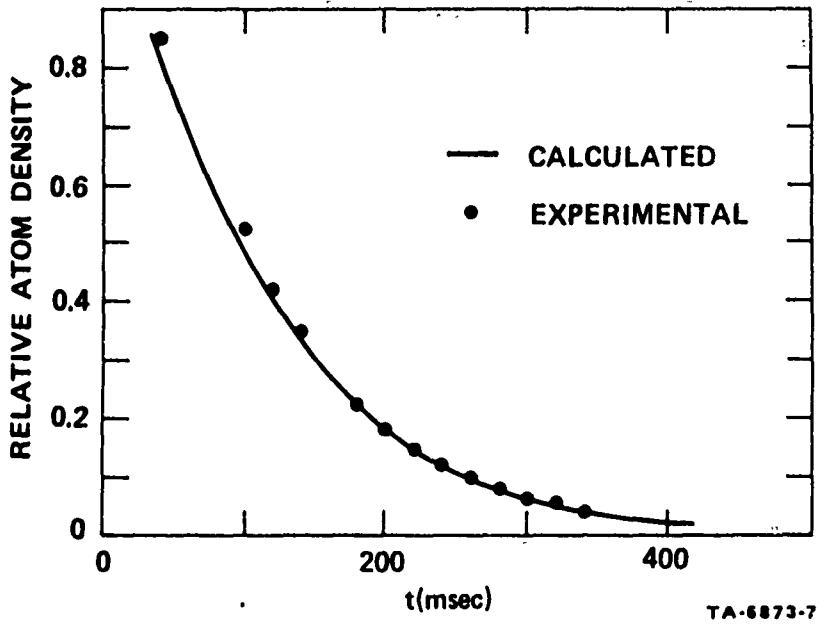
Figure 4   COMPARISON OF CALCULATED AND EXPERIMENTAL
ATOM DENSITIES DURING A TRANSIENT EXPERIMENT
P_{TOTAL} = 2.10 torr, x = 15 cm)
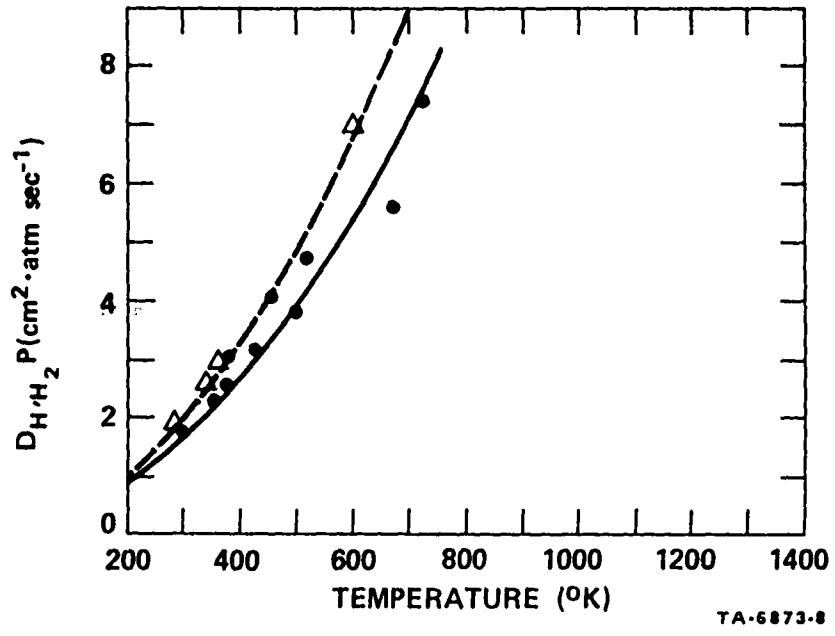
Figure 5   VARIATION OF DIFFUSION COEFFICIENT D_{H,H_2}
WITH TEMPERATURE [--- exp-6, ref. 3; -- exp-6:
ϵ/k = 16.7°K, a = 12.45, r_m = 3.90 A; △ L.-J.(6—12)
ref. 1; ● EXPERIMENTAL DATA, TABLE 2]

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13. ABSTRACT

The multicomponent diffusion coefficient D_{H,H_2} has been evaluated from measurements of the relative atom density in a semi-infinite catalytic cylinder as a function of (a) distance from the atom source under steady-state conditions, and (b) time during the transient condition associated with removal of the atom source after attainment of steady state. An electron spin resonance spectrometer was employed for atom-density measurements and a radio-frequency discharge for atom production in the total gas-pressure range from 0.85 to 2.6 torr. The value for the diffusion coefficient was found to be $D_{H,H_2} = 1.8 \pm 0.13 \text{ cm}^2 \cdot \text{sec}^{-1}$ at 1 as a function of temperature (293 to 719°K) are analyzed in terms of different interaction potentials for the atom-molecule collision.

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
diffusion coefficient						
atom						
catalytic cylinder						